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(54) Title: PRECIPITATION HARDENED FERROUS ALLOY WITH QUASICRYSTALLINE PRECIPITATES (57) Abstract According to the invention a precipitation hardened metallic alloy is provided, in which the strengthening is based on the precipitation of particles and wherein the particles have a quasicrystalline structure, said structure being essentially maintained at aging times up to 1000 h and tempering treatments up to 650 °C, the strengthening involving an increase in tensile strength of at least 200 MPa. ...		

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PRECIPITATION HARDENED FERROUS ALLOY WITH QUASICRYSTALLINE PRECIPITATES

5 The present invention is concerned with the class of metal alloys in which the mechanism described below can be used for strengthening. More especially, the mechanism is based on the precipitation of particles. In particular, the concern is with the class of metal alloys in which strengthening is based on the precipitation of particles having a quasicrystalline structure.

10 One of the objectives with the invention is to assess a precipitation hardening mechanism in metal alloys which gives rise to an unusually high hardening response in strength, not only compared with other precipitation hardening mechanisms, but also compared with other hardening mechanisms for metal alloys in general.

15 Another objective is to assess a precipitation hardening mechanism which involves not only a high hardening response, but also offers a unique resistance to overaging, i.e. conditions which allow the high response in strength to be sustained for a long time, even at relatively high temperatures. This means that softening can be avoided in practice.

25 An additional objective of the invention is to assess, for a class of metal alloys, a precipitation hardening mechanism, which does not require a complicated processing of the metal alloy or a complicated heat treatment sequence, in order to enable the precipitation of quasicrystal particles resulting in a high hardening response in strength and a high resistance to overaging. Instead the precipitation hardening can be performed in a metal alloy produced according to normal practice and the heat treatment can be performed as a simple heat treatment at a relatively low temperature.

30 Other objectives of the invention will in part be obvious and in part pointed out during the course of the following description.

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Traditionally, there is a number of various types of precipitation hardening mechanisms used in metal alloys. There is for instance precipitation of different types of carbides in high speed steel, precipitation of intermetallic phases such as e.g. η -Ni₃Ti or β -NiAl in precipitation hardenable stainless steels, precipitation of intermetallic phases such as θ -CuAl₂ in aluminium alloys and γ -CuBe in copper based alloys. These types of crystalline precipitates often give a significant contribution to strength, but they suffer from being sensitive to overaging which implies that loss of strength can be a problem for aging times above about 4h. All these types of precipitation hardening mechanisms are basically similar; the hardening is based on the precipitation of a phase or particle with a perfectly crystalline structure.

Quasicrystals have structures that are neither crystalline nor amorphous but may be regarded as intermediate structures with associated diffraction patterns that are characterised by, among others, golden ratio between the length of adjacent lattice vectors, five-fold orientation symmetries and absence of translation symmetries. Such structures are well-defined and their characteristics together with the results from various investigations of the conditions under which quasicrystals form have been summarized in an overview by Kelton (1). The presence of quasicrystalline structures has mostly been reported in materials, which have been either rapidly quenched from a liquid state or cooled to supersaturation (e.g. 2,3). The materials have in these cases therefore not reached thermodynamic equilibrium or even metastability. Moreover, there is no report on the possibility of using quasicrystalline precipitation in a thermodynamically stable structure as a hardening mechanism in metal alloys produced according to normal metallurgical practice.

A purpose of the described research was therefore to invent a precipitation hardening mechanism, which can be employed in commercial metal alloy systems such as iron-based materials and which is superior to the previously known hardening mechanisms

which are all based on the precipitation of a crystalline type of phase or particle. It will not require any complicated processing of the material or any complicated heat treatment procedure during the hardening. It will involve precipitation of particles which are precipitated from a material with a normal crystalline structure. This also implies that rapid quenching from a liquid state or supersaturation of the material is not required for the precipitation to take place. The class of metal alloys in which the invented precipitation hardening mechanism should be possible to use ought to be suitable to be processed in the shape of wire, tube, bar and strip for further use in applications such as dental and medical instruments, springs and fasteners.

The experimental iron-based material used to demonstrate this mechanism was a so called maraging steel, i.e. a type of precipitation hardenable stainless steel, with the following composition in wt%:

Table of chemical composition of the experimental material (wt%)

C	Si	Mn	Cr	Ni	Mo	Ti	Cu	Other elements	Rest
.009	.15	.32	12.20	8.99	4.02	.87	1.95	< .5	Fe

The material was produced according to normal metallurgical practice in steel industry in a full scale HF furnace and hot rolled down to wire rod of 5.5 mm diameter followed by cold drawing down to wire of 1 mm diameter, including appropriate intermediate annealing steps. This resulted in a large volume fraction of martensite. Homogenization of the distribution of alloying elements was reached by a so called soaking treatment well above 1000°C, i.e. at temperatures where, for all practical purposes, the microstructure may be regarded as being in an equilibrium condition.

Samples in the form of 1 mm diameter wire were heat treated in the temperature range 375-500°C and subsequently examined using analytical transmission electron microscopy (ATEM) in a microscope of the type JEOL 2000 FX operating at 200 kV,

provided with a LINK AN 10 000 system for energy dispersive X-ray analysis. High resolution electron microscopy (HREM) was performed in a JEOL 4000 EX instrument operating at 400 kV, provided with a top entry stage.

5

Thin foils for ATEM were electropolished at a voltage of 17V and a temperature of -30°C using an electrolyte of 15% perchloric acid in methanol. It was found that diffraction analysis of precipitates was facilitated when the matrix was removed as is the case in extraction replicas. Extraction replicas were obtained by etching in a solution of 12.5 g Cu_2Cl , 50 ml ethanol and 50 ml HCl followed by coating with a thin layer of carbon. The replica was stripped from the specimen by etching in 5% Br and water-free methanol.

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Extraction of residue for structural analysis was carried out in a solution of 394 ml HCl in 1500 ml ethanol. Extracted residue was examined in a Guinier-Hägg XDC 700 X-ray diffraction camera. The residue was also applied on a perforated carbon film and subsequently analysed in a HREM.

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Fourier transformation of small areas in the HREM images was carried out in a system termed CRISP (4). The aim of these experiments was to perform diffraction analysis of extremely small areas, i.e. areas that were much smaller than the size of the smallest selected area aperture available.

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Aging at 475°C resulted in the instantaneous precipitation of particles. After 4h the particles had grown to a diameter of typically 1 nm. After aging at 475°C for 100h the particles had grown to a size of 50-100nm, an example of which is given in Fig 1. Further aging at this temperature showed no sign of particle growth up to a total aging time of 1000h. Since 1000h is an unusually long aging time there is reason to believe that the particles have already reached their stable crystallography and that no crystallographic transformation of the particles will occur. This indicates that the particles are extremely resistant to overaging. A thorough

30

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investigation of the microstructure using ATEM showed that the majority of precipitates had the same crystallographic structure, viz a quasicrystalline structure as will be described in detail below.

5 Analysis of diffraction patterns from such particles showed absence of translation symmetry indicating that the particles are not perfectly crystalline. A series of diffraction patterns taken in various directions in the crystal showed that it was possible to obtain patterns with symmetries that are characteristic of quasicrystals. Measurements of
10 the ratio between the length of reciprocal lattice vectors showed values close to 1.62, which is in good agreement with the golden ratio found in quasicrystals (1). An example of a diffraction pattern showing both five-fold symmetry and golden ratio between the absolute values of lattice vectors (indicated by arrows) is shown in
15 Fig 2.

As in the case of quasicrystalline structures, five-fold symmetries can be produced in diffraction patterns from twinned structures. In order to exclude the possibility of twinning, a thorough investigation
20 of the microstructure was performed in a HREM. Images at atomic resolution were digitized and Fourier transformed. The diffraction patterns obtained from very small areas using this method showed perfect agreement with the diffraction patterns obtained using conventional diffraction of larger areas, thereby proving that
25 twinning is not the cause of five-fold symmetry in the present case. This conclusion was further confirmed by employing the inverse Fourier transform of already transformed patterns whereby no twinning could be observed in the real image thus obtained.

30 Chemical analysis using energy dispersive X-ray analysis of the quasicrystalline particles showed a typical chemical composition of 5% silicon, 15% chromium, 30% iron and 50% molybdenum. It was concluded from the investigation of the present experimental steel that molybdenum and chromium were necessary alloying elements to
35 obtain precipitation of quasicrystals in iron-base alloys.

Quasicrystals in metals and alloys are usually formed during rapid quenching from the liquid state (1). This was first reported in 1984 for an Al-14%Mn alloy (5). There are also reports on the solid state formation of quasicrystals in supersaturated rapidly quenched alloys (6). However, there are very few reports of the formation of quasicrystals in conventionally produced alloys during an isothermal heat treatment in the solid state. The only report of such an observation that has been found is from a ferritic-austenitic steel (7). These authors found quasicrystalline phases after extremely long tempering times, viz. 1000h or more. However, these phases were not associated with precipitation strengthening. The present invention is therefore unique in the sense that it involves the isothermal formation of quasicrystalline precipitates that are used for precipitation strengthening of conventionally produced alloys and metals in the solid state. By strengthening is here meant an increase in tensile strength with at least 200 MPa or usually at least 400 MPa as a result of a thermal treatment.

There are at least two advantages of using quasicrystals as strengthening objects during tempering. Firstly, the strengthening effect is higher than for crystalline precipitates owing to the difficulty of dislocations to move through a quasicrystalline lattice. Secondly, precipitate growth above a certain size is very difficult since large quasicrystals are difficult to form. Both these statements are confirmed by the observations in the present study since the strengthening effect and the resistance to overaging in the experimental steel are extremely high. In fact, no evidence of softening was observed during tempering experiments up to temperatures of 500°C and times of 1000h, as can be seen in Table 1. Furthermore, the strength increment during tempering is usually about 800 MPa and can in extreme cases be as high as 1000 MPa, which is quite a remarkable result.

An example of the hardening response under comparable conditions in the same temperature range using a precipitation reaction in a conventional maraging steel of a composition in accordance with US

Patent no. 3408178 is given in Table 1 for comparison. This is an example of softening behaviour typical of a crystalline precipitation reaction.

5 Thus it can be concluded that the above-mentioned hardening mechanism involving precipitation of quasicrystalline particles gives rise to an exceptionally high strength increment during tempering in combination with a resistance to overaging that is unique among alloys in general. These properties are intimately related to the precipitates being quasicrystalline and cannot be expected in
10 association with conventional precipitation since crystalline precipitates are much more deformable and are likely to undergo coarsening in accordance with the so called Ostwald ripening mechanism. In the present alloy system precipitation of quasicrystals occurred in the martensitic matrix. It is therefore concluded that the
15 said mechanism is favoured by a martensitic or the closely related ferritic structure both of which for practical purposes can be regarded as body centered cubic (bcc) structures. It is expected that the said mechanism can occur also in other structures such as face
20 centred cubic (fcc) and close packed hexagonal (cph) structures. This hardening mechanism has been demonstrated to occur in the temperature interval 375-500°C but since this mechanism is dependent on the alloy composition it can be expected to occur in a much wider range in general, viz. below 650°C. Usually,
25 temperatures below 600°C are expected to be used or, which is preferred in practice, temperatures below 550°C or 500°C. A recommended minimum temperature is in practice 300°C, or preferably 350°C. The tempering treatment can be performed isothermally but tempering treatments involving a range of various
30 temperatures can also be envisaged. In the present case at 475°C it was found that the quasicrystalline particles had reached a typical diameter of 1 nm after 4h and a typical diameter of 50-100 nm after 100h, after which no substantial growth occurred. A particle diameter typically in the range 0.2-50 nm is expected after 4h while diameters
35 typically in the range 5-500 nm are expected after 100h. It is expected that a minimum of 0.5 wt% molybdenum or 0.5 wt%

5 molybdenum and 0.5 wt% chromium, or at least 10 wt% chromium in stainless steels, is required to form quasicrystalline precipitates as a strengthening agent in iron-base steels or iron group alloys. The experimental steel used to demonstrate the strengthening potential of stainless steels and to show the unique properties of quasicrystals can be regarded as a conventional stainless steel in the sense that only conventional alloying elements are present and in the sense that also conventional crystalline precipitation can occur in various amounts, both within the temperature range where quasicrystals are formed, and outside this range. It should be emphasized that quasicrystalline precipitates was the major type of precipitate in the present steel below 500°C. Above 500°C, the fraction of quasicrystalline precipitates diminished and gradually became a minority phase, the majority being crystalline precipitates. In general, it can be expected that the described mechanism can occur in a rather wide range of tempering temperatures employed in practice where crystalline precipitation normally takes place. i.e. below temperatures of approximately 650°C. It can also be expected to occur in all other alloy systems in which quasicrystals have been observed to form under cooling. Quasicrystalline precipitation is thus expected to give rise to precipitation hardening in a wide variety of alloy systems other than steels and iron-base alloys, such as copper-, aluminium-, titanium- zirconium- and nickel-alloys, wherein the minimum amount of base metal is 50%. In the case of iron group alloys the sum of chromium, nickel and iron should exceed 50%.

30 In the manufacture of medical and dental as well as spring or other applications an alloy with a precipitation mechanism according to the invention is used in the making of various products such as wire in sizes less than Ø15 mm, bars in sizes less than Ø70mm, strips in sizes of thickness less than 10 mm and tubes in sizes with outer diameter less than 450 mm and wall thickness less than 100 mm.

References

1. K. F. Kelton, International Materials Reviews, **38**, no. 3, 105, 1993.
2. EP O 587 186 A1.
- 5 3. EP O 561 375 A2.
4. S. Hovmöller, Ultramicroscopy, **41**, 121, 1992.
5. D. Schechtman, I. Blech, D. Gradias and J.W. Cahn, Phys. Rev. Lett., **53**, 1951, 1984.
6. P. Liu, G. L. Dunlop and L. Arnberg, International J. Rapid
10 Solidification, **5**, 229, 1990.
7. Z. W. Hu, X. L. Jiang, J. Zhu and S. S. Hsu, Phil. Mag. Lett., **61**,
no. 3, 115, 1990.

Table 1.

HARDNESS HV1

Time (min)	Tempering temperatures					
	Experimental steel				US Patent 3408178	
	375°C	425°C	475°C	500°C	475°C	500°C
0.01	427	427	427	427	321	321
0.2	473	489	543	585	402	420
0.6	474	501	566	592	416	436
1	479	507	577	609	428	465
2	485	524	584	610	450	493
4	503	542	631	612	482	517
6	523	550	616	617	482	526
12	511	587	636	623	525	538
20	532	590	630	625	538	533
36	534	608	657	622	545	549
60	535	631	636	631	567	571
120	533	649	654	628	563	556
240	591	636	660	650	567	533
480	604	655	660	665	567	540
960	620	655	660	665	561	533
1920	664	675	681	677	558	515
3840	681	681	699	645	542	519
6000	679	716	680	658	545	495
10100	703	717	697	659	527	475
20200	730	731	694	659	509	463

CLAIMS

- 5 1. A precipitation hardened alloy based on iron, in which the strengthening is based on the precipitation of particles, characterized in, that the particles have a quasicrystalline structure, said structure being essentially maintained at aging times up to 1000h and tempering treatments up to 650°C, the strengthening involving an increase in tensile strength of at least 200 MPa.
- 10 2. A precipitation hardened alloy according to claim 1, characterized in, that it is based on chromium, nickel and iron, the sum of said elements exceeding 50%.
- 15 3. A precipitation hardened alloy according to any of the preceding claims characterized in, that it is based on iron or a combination of iron, chromium and nickel having a minimum content of 0.5% by weight of molybdenum.
- 20 4. A precipitation hardened alloy of any preceding claim wherein the tempering treatment is in the range 300-650°C.
5. A precipitation hardened alloy of any preceding claim being used in the manufacture of medical and dental applications.
- 25 6. A precipitation hardened alloy of any of claims 1-5 being used in the production of wire in sizes less than Ø15 mm.
7. A precipitation hardened alloy of any of claims 1-5 being used in the production of bars in sizes less than Ø70 mm.
- 30 8. A precipitation hardened alloy of any of claims 1-5 being used in the production of strips in sizes less than a thickness of 10 mm.
- 35 9. A precipitation hardened alloy of any of claims 1-5 being used in the production of tubes in sizes with outer diameter less than 450 mm and wall thickness less than 100 mm.

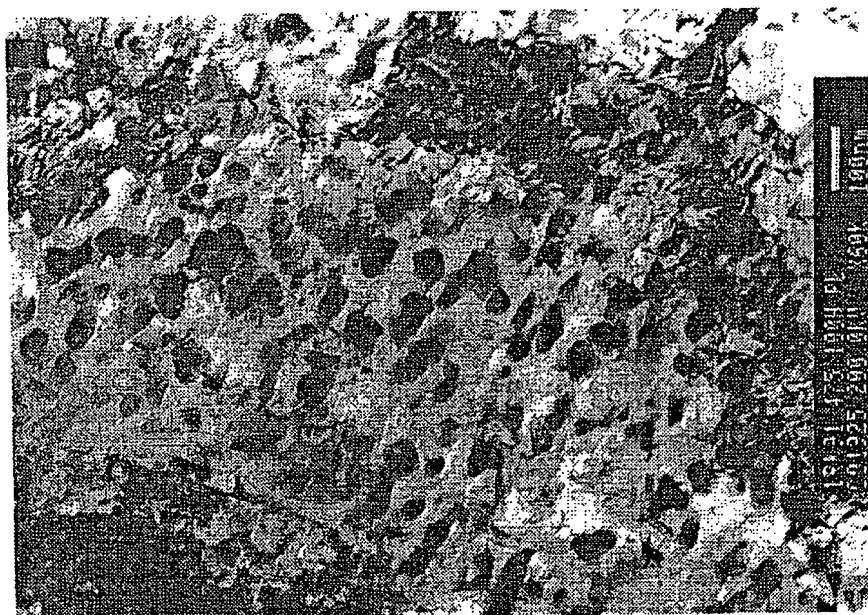


Figure 1

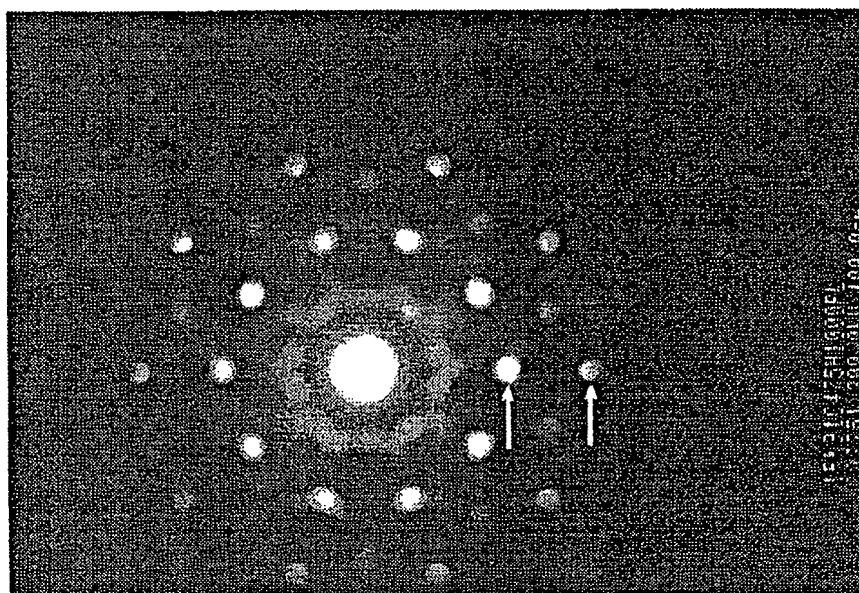


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 94/00921

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C21D 6/02, C22C 38/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C21D, C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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WPAT, CLAIMS, USPM, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0561375 (MASUMOTO, TSUYOSHI), 22 Sept 1993 (22.09.93) --	1-9
P,A	EP, A1, 0587186 (YOSHIDA KOGYO CO., LTD.), 16 March 1994 (16.03.94) --	1-9
A	INTERNATIONAL MATERIALS REVIEWS, Volume 38, No 3, 1993, K.F. Kelton, "Quasicrystals: structure and stability" page 131, column 2, line 10 - page 132, column 2, line 2 ----- --	1-9

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

31/12/94

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0561375	22/09/93	JP-A- 6041702	15/02/94
EP-A1- 0587186	16/03/94	NONE	